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GUANIDINE AND ITS NITROGEN DERIVATIVES

A Thesis

Presented to the Faculty of the Graduate School of Cornell University for the degree of Masters of Science in Engineering

By

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BIOGRAPHICAL SKETCH

The author was born in Stevens Point, Wisconsin on June 5, 1921. He attended elementary school in Berlin, Wisconsin; entered Berlin High School and graduated from there in June, 1938. For a year, he worked at the Quality Sausage Company, Berlin, Wisconsin as a meat cutter and clerk. He entered Central State Teachers College, Stevens Point, Wisconsin, in September, 1939; and received a Bachelor of Science degree, with majors in Chemistry and Mathematics and minor in Physics, in May, 1943.

He went on active duty in the U.S. Naval Reserve May 31, 1943; reported to the U.S. Naval Reserve Midshipmen's School, Notre Dame University, South Bend, Indiana, where he completed the course of instruction and was commissioned as Ensign September 22, 1943. Immediately he reported to the Sub-Chaser Training Center, Miami, Florida, to attend a course in anti-submarine warfare. Upon completion, he reported to the USS Harold C. Thomas (DE 21) in the Pacific area.

On July 1, 1945, he reported to the postgraduate school, U.S. Naval Academy, Annapolis, Maryland, for a course of instruction in Ordnance Engineering (Explosives). He was selected as one in a group of fifteen to attend Cornell University for the completion of the course.

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INTRODUCTION

The interest and work on guanidine and its derivatives in the past decade has been greatly stimulated by their increased uses. Of many of its derivatives, nitroguanidine is of peculiar interest, both technically and scientifically. The compound is an explosive and for this reason many practical applications can be found for it. Since it may be prepared from dicyandiamide, a derivative of lime-nitrogen (calcium cyanamide), the essential raw materials for which are nitrogen of the air and limestone, the potential supply is unlimited. It is important scientifically, for from it aminoguanidine, hydrazine, hydronitric acid, and other products, may be obtained from its reduction. As an example of the use of these compounds, aminoguanidine is being diazotized and hot-coupled with various intermediates to furnish a whole new series of azo dyes which possess good dyeing properties on animal fibers.

Strecker, in 1861, first obtained guanidine as an oxidation product of guanine. Since that time, various men have studied the properties and reactions of guanidine and its derivatives. Some of the more recent work has been done by Davis, whose work covered guanidine, nitroguanidine, guanidine nitrate, and the alkyl substituted guanidines.

GUANIDINE

Guanidine is an imide of urea or the imidine of carbamic acid. In its free state, it occurs only in a few plants, but its derivatives are widely distributed. It occupies a unique position among the organic bases, for it alone approximates the strong alkalies in basic strength. Calculations and measurements have been made by Davis and Elderfield (6) to show that guanidine is a strong base and electrolyte. To determine the ratio of strength of guanidonium hydroxide to that of sodium hydroxide, the following tests were used:

(1) Observing the rate of change of the angle of rotation of a hyoscyanine solution in the presence of the two bases.

(2) Relative rates of saponification with ethyl acetate.

(3) Depression of the freezing point of water. The ratios of guanidonium hydroxide to sodium hydroxide obtained were 0.78 to 1, 0.85 to 1, and 0.81 to 1, respectively. Also the heat of neutralization of guanidine, 14.12 kilogram calorie per gram mole, which is only slightly less than the constant value for strong bases. Guanidine is a base of the order of strength of potassium hydroxide.

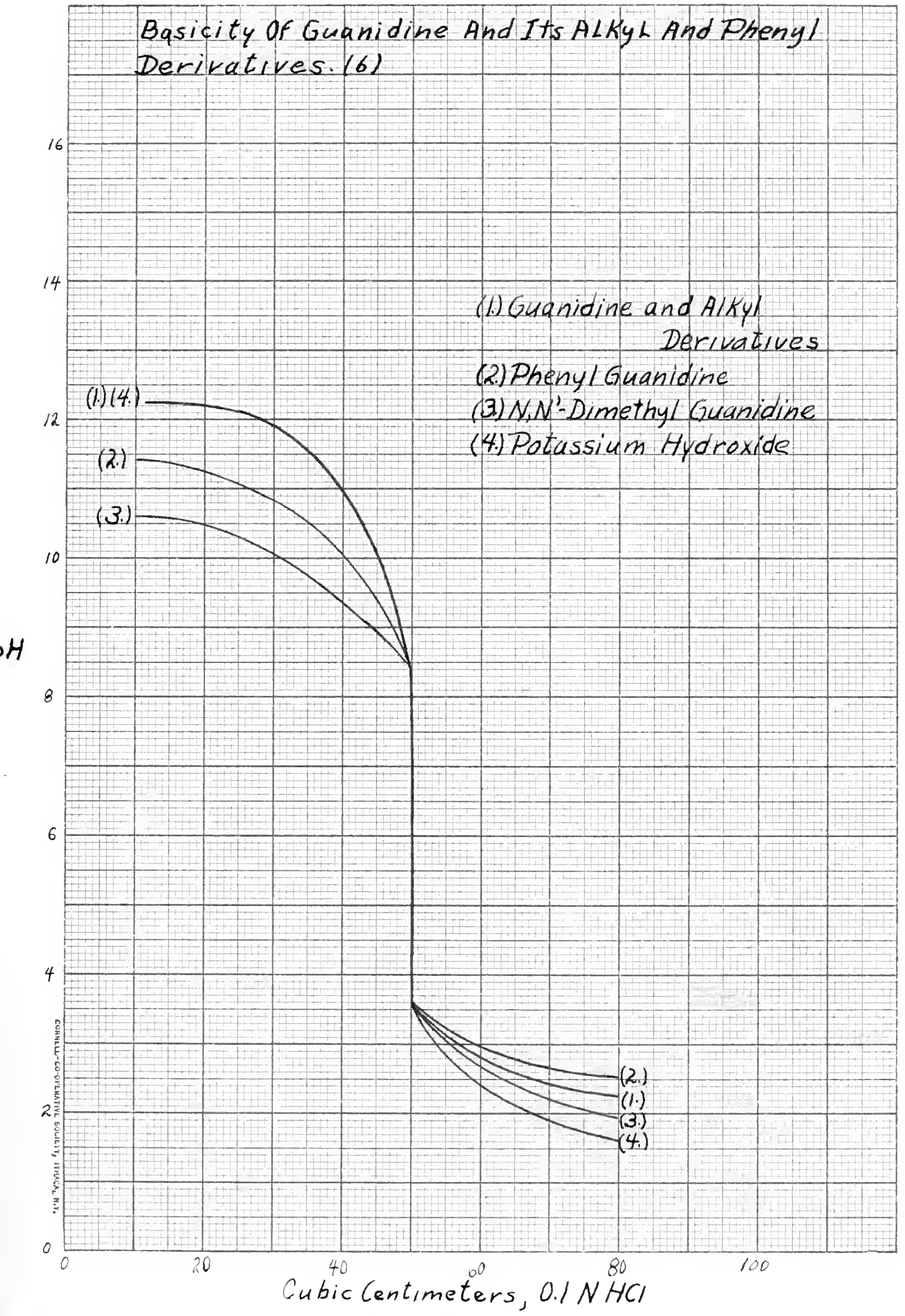
Basicity Of Guanidine And Its Alkyl And Phenyl Derivatives. (6)
(1.) Guanidine and Alkyl Derivatives
(2.) Phenyl Guanidine
(3.) N,N'-Dimethyl Guanidine
(4.) Potassium Hydroxide
(1.)(4.)
(2.)
(3.)
pH
16
14
12
10
8
6
4
2
0
0
20
40
60
80
100
Cubic Centimeters, 0.1 N HCl
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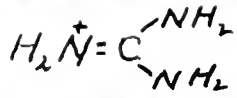
Fig. I

Introduction of a single alkyl substituent is without much effect on the basicity of the parent compound. When two alkyl groups are introduced, the substance becomes less basic. The introduction of an aromatic substituent also tends to lower the basicity. Davis and Elderfield determined the basicity of guanidine, of several of its substituted alkyl derivatives, and of phenyl guanidine. The change of pH of the base with the amount of hydrochloric acid added to it provided a convenient means for comparing the basicity of these compounds (Fig. I).

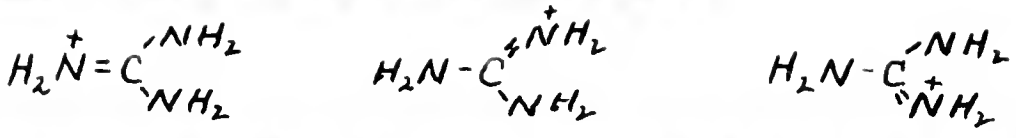
The pure salts of guanidine can be obtained readily, especially the carbonate which crystallizes well, but the free base is not easy to prepare. One method used to get the pure compound from the salt is to mix an alcoholic solution of guanidine perchlorate and potassium hydroxide, remove the insoluble potassium perchlorate by filtration, and evaporate the remaining filtrate to dryness in a vacuum over phosphorus pentoxide. The free base forms a colorless, caustic, and very hygroscopic mass of crystals that melt indistinctly at 50° C. and decompose at higher temperature in a polymerization reaction to form melamine. It is stable in aqueous solution and is a monoacid base with basicity as previously described. It forms stable salts with weak acids, as boric and silicic acids.

The structure of the guanidine kation or guanidonium

ion has been shown by Lecher and Graf (17) to be:



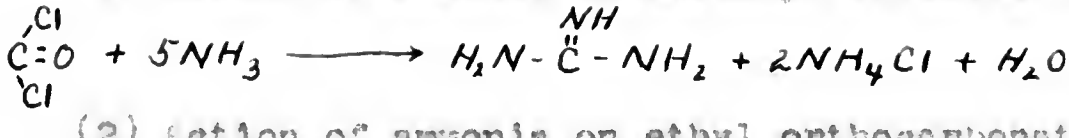
Davis, Yelland, and Ma (9) have shown that the proton goes to the imide nitrogen but the charge shifts to the carbon atom. The former seems the most likely case , however, due to the properties of the ion. X-ray analysis shows that the three nitrogen atoms are symmetrically placed around the carbon atom at a distance less than that for a normal nitrogen-carbon double bond. This must be because all three nitrogen atoms are taking part in a resonance. Since the double bond can be in all three possible positions, three structures may partake in the resonance hybrid. These three structures are:



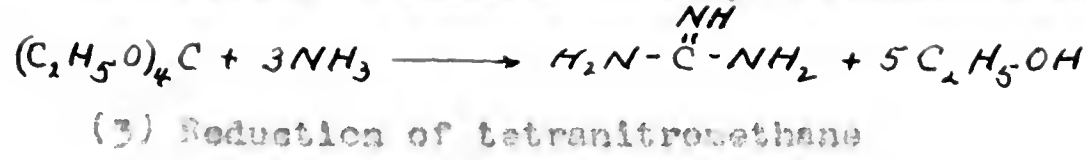
The properties of guanidine are therefore due not to one structure alone but to all three structures in the hybrid.

Several synthesis have been developed for the preparation of guanidine. Among these are:

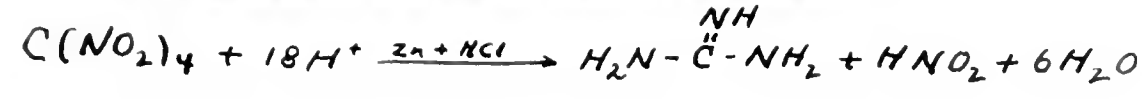
(1) Action of ammonia on carbonyl chloride (phosgene)

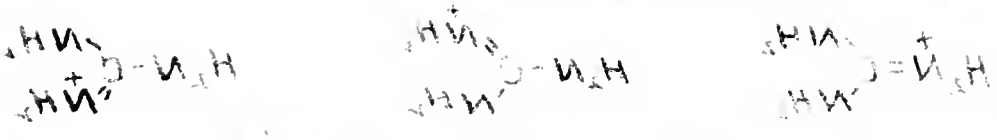


(2) Action of ammonia on ethyl orthocarbonate



(3) Reduction of tetranitromethane





(4) Addition of ammonia to cyanamide

$$H_2N-CN + NH_3 \longrightarrow H_2N-\overset{NH}{\overset{\|}{C}}-NH_2$$

(5) Addition of ammonia to chloropicrin

$$Cl_3CNO_2 + 3NH_3 \xrightarrow[H_2O]{150^\circ} H_2N-\overset{NH}{\overset{\|}{C}}-NH_2 + HNO_2 + 3HCl$$

(6) Interaction of carbontetrabromide with alcoholic ammonia in a sealed tube at 100° C

$$CBr_4 + 4NH_3 \longrightarrow H_2N-\overset{NH}{\overset{\|}{C}}-NH_2 + NH_4Br + 3HBr$$

(7) Interaction of cyanogen iodide with alcoholic ammonia in a sealed tube at 100° C

$$I-CN + 2NH_3 \longrightarrow NH_2-CN + NH_4I \; ; \; NH_2-CN \xrightarrow{NH_3} H_2N-\overset{NH}{\overset{\|}{C}}-NH_2$$

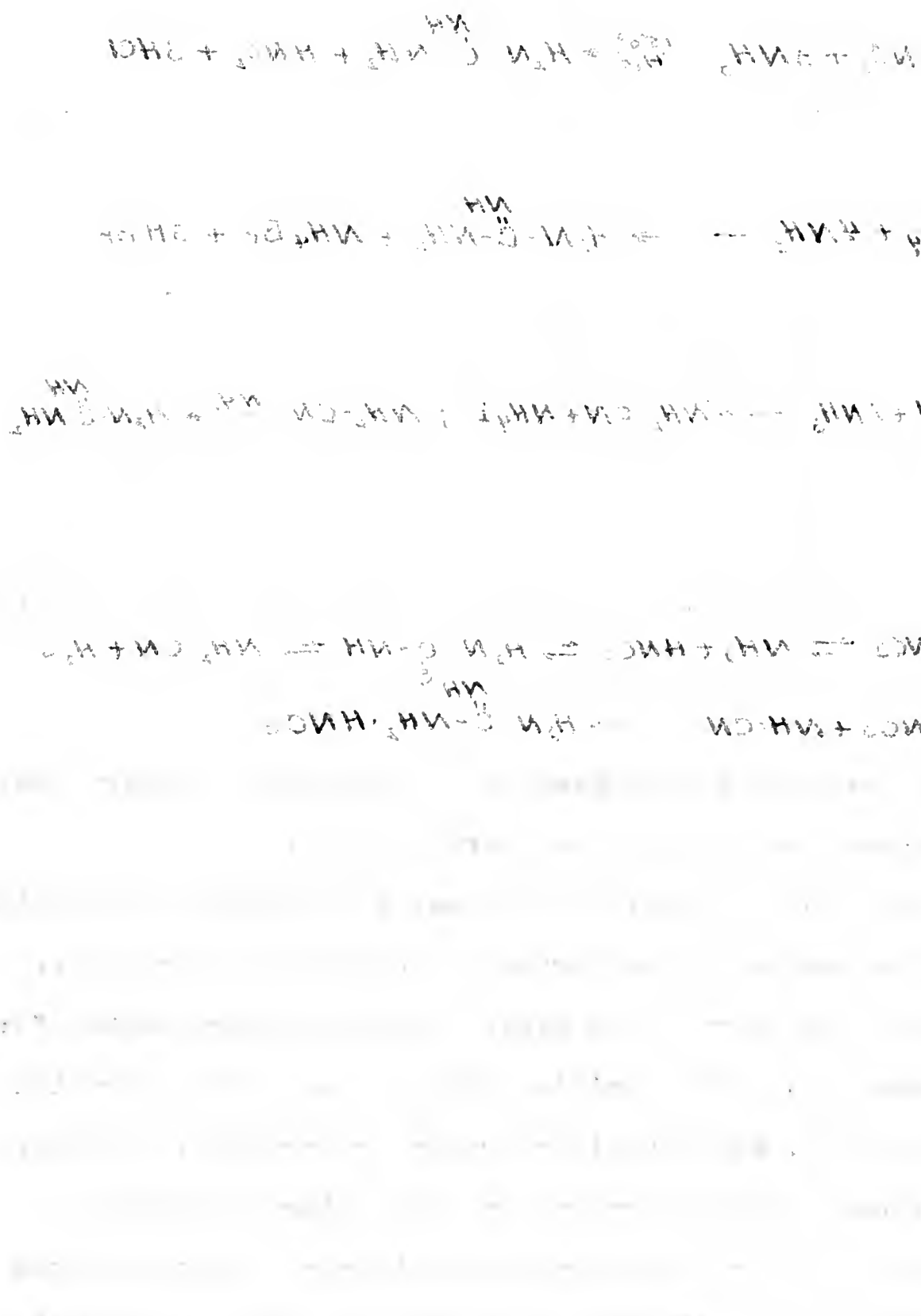
(8) Heating ammonium thiocyanate at 170°-190° C for twenty hours or until hydrogen sulfide no longer comes off. The yield in this process is excellent.

$$NH_4NCS \rightleftharpoons NH_3 + HNCS \rightleftharpoons H_2N-\underset{\underset{S}{\|}}{C}-NH \rightleftharpoons NH_2-CN + H_2S$$

$$NH_4NCS + NH_2CN \longrightarrow H_2N-\overset{NH}{\overset{\|}{C}}-NH_2 \cdot HNCS$$

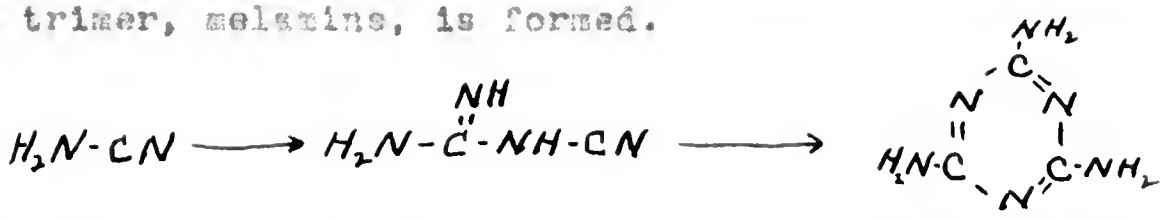
Only a few of the syntheses are on commercial importance; the others are merely laboratory methods.

The process involving the use of ammonium thiocyanate, which is eventually converted to guanidine thiocyanate, was for many years the easiest and most common method for the preparation of guanidine salts. On direct nitration of the salts, nitroguanidine could be prepared. However, the nitroguanidine prepared by this method contained traces of sulfur compounds which attacked nitrocellulose and affected the stability of smokeless powder. This is



one of the reasons why the use of nitroguanidine in smokeless powder did not come into earlier use.

The process involving the use of cyanamide proved to be more practical because of the availability of calcium cyanamide as a raw material. Cyanamide itself is not a suitable raw material because of the difficulties in preparation, purification, and storage. It is a colorless crystalline substance, melting at 40° C, and is soluble in water, ether, and alcohol. It polymerizes readily upon evaporation of an aqueous solution to produce a dimer, dicyandiamide; on heating or long standing a trimer, melamine, is formed.



Melamine has extensive use in the plastics industry. It polymerizes with formaldehyde and urea to form a resin used for adhesives and molding powders.

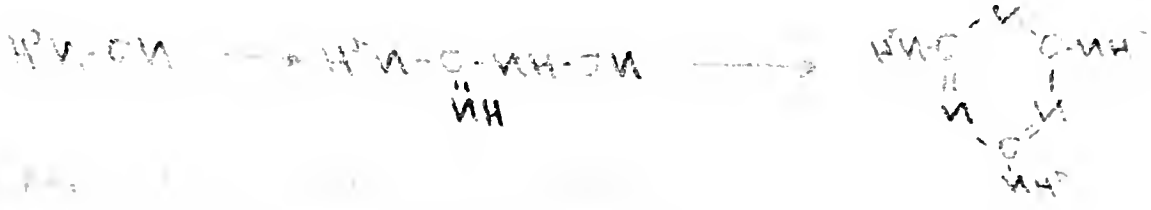
The earlier method for the commercial preparation of cyanamide was by treating potassium cyanide with a halogen, usually chlorine or bromine, to form cyanogen halide, then treating with a solution of ammonia in water or in ether.

$$KCN + X_2 \longrightarrow KX + X\text{-}CN$$

$$2NH_3 + X\text{-}CN \longrightarrow NH_4X + NH_2\text{-}CN$$

$$XNH^3 + X\text{-}CN \longrightarrow NH^4X + NH^2\text{-}CN$$

$$XCN + X^2 \longrightarrow XX + X\text{-}CN$$



If the reaction is carried out in ether solution, the ammonium chloride precipitates and can be filtered off. The ether is evaporated spontaneously, leaving the cyanamide as a syrup which may be crystallized by standing over sulfuric acid in a desiccator. Cyanamide may also be prepared by removing hydrogen sulfide from thiourea with mercuric oxide or removing water from urea with thionyl chloride.

$$H_2N-\overset{S}{\overset{\|}{C}}-NH_2 + HgO \longrightarrow NH_2-CN + HgS + H_2O$$

$$H_2N-\overset{O}{\overset{\|}{C}}-NH_2 + SOCl_2 \longrightarrow NH_2-CN + SO_2 + 2HCl$$

The production of cyanamide (14) from calcium carbide by nitrogen fixation has made it more readily available for commercial synthesis. When calcium carbide containing a little calcium flouride as a catalyst is brought in contact with gaseour nitrogen at a temperature of about 1000° C, the following reaction takes place:

$$CaC_2 + N_2 \longrightarrow CaNCN + C + 91,800 \text{ Calories}$$

The calcium carbide is made from coke and limestone in a smothered arc furnace:

$$2CaCO_3 + 5C \longrightarrow 2CaC_2 + 3CO_2$$

The carbide is then crushed and ground to a fine powder. All operations are carried out in a nitrogen atmosphere, for in contact with moist air, acetylene would be produced and form an explosive mixture. The finely ground carbide is run into an oven with a capacity of about 8000 pounds and covered. The charge is heated from the center by a carbon resistance rod and the nitrogen, from liquid air, is passed upward through the charge. Since the reaction exothermic, heating is necessary only during the first part of the run. The formation of crude calcium cyanamide requires not more than forty hours. The contents of the oven forms a solid block which is lifted out and cooled. The crude product contains about sixty per cent of calcium cyanamide, the remainder being quicklime, carbon and a little unchanged calcium carbide. The block is pulverized and the carbide is decomposed by water. The resulting dark-colored mixture of calcium cyanamide, lime, and carbon is known as "lime nitrogen" or "kalkstickstoff", and is a very common fertilizer.

Calcium cyanamide has none of the poisonous action of prussic acid and its salts, although it dilates the blood vessels and thus vastly increases the effect of substances such as alcohol or caffeine on the system. Besides the use of this compound in agriculture, it has been used as a source of urea and certain cyanides.

To produce cyanamide, the calcium cyanamide is hydrolysed with water. If water alone is used, some soluble cyanamide is produced, and some calcium hydrogen cyanamide is also formed. This is a white microcrystalline sparingly soluble substance. Addition of a slight amount of acid to the water converts the calcium salt to a solution of cyanamide with a precipitate of the inorganic salt. The acids usually used are sulfuric, oxalic, or carbonic. Carbonic acid is the best for the hydrolysis reaction.

$$2CaNCN + 2H_2O \longrightarrow Ca(OH)_2 + Ca(NH\text{-}CN)_2$$

$$Ca(NH\text{-}CN)_2 + CO_2 + H_2O \longrightarrow CaCO_3 + 2NH_2CN$$

The solution formed is directly applicable in certain reactions, as for example, the preparation of various guanidine salts. One of the more recent uses has been for the preparation of guanidine phosphate, which has possibilities as a fertilizer because of the presence of phosphorous and nitrogen, both of which are necessary for plant growth. (12) In hydrolysis of the solution with ammonium sulfide, the hydrogen sulfide of the molecule takes part in the reaction to form thiourea. This reaction is used to produce many tons of thiourea for the rubber industry. Urea can be prepared from the solution by hydrolysis with sulfuric acid; in

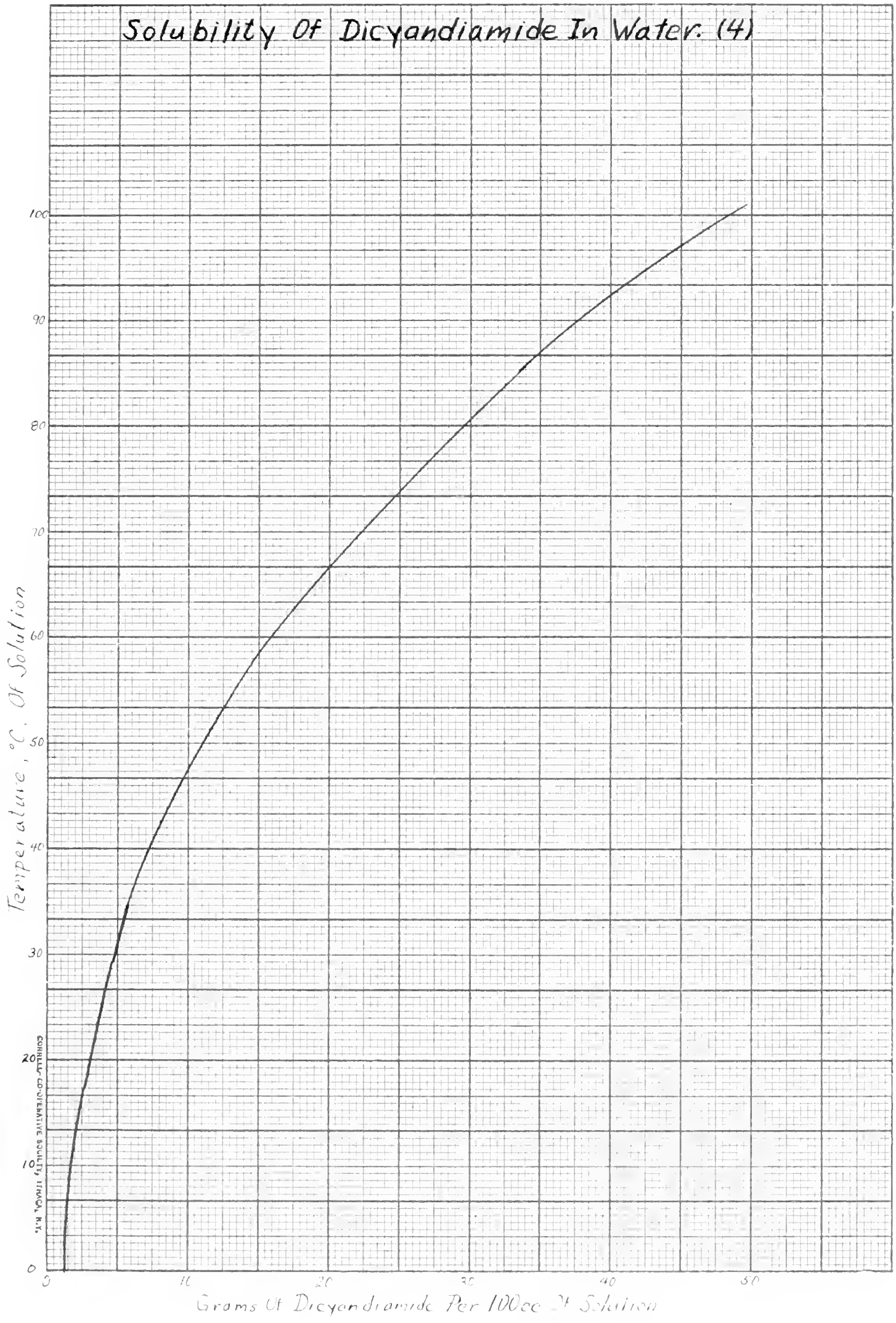

Solubility Of Dicyandiamide In Water. (4)
Temperature, °C. Of Solution
Grams Of Dicyandiamide Per 100cc Of Solution
0
10
20
30
40
50
60
70
80
90
100
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Fig. II

fact, it may be prepared directly from calcium cyanamide by using sulfuric acid as the hydrolyzing agent and allowing the reaction to go beyond the cyanamide stage.

On evaporation of the cyanamide solution, dicyandiamide is formed. This is a convenient source of starting material for the preparation of guanidine nitrate. Dicyandiamide crystallizes from water, being soluble at about one part in one hundred at 0° C and about 47 parts in 100 at 100° C. (Fig. 11) The crystals are flat needles or plates which melt at 208° C and decompose when heated above the melting point. It is used directly in the preparation of various guanidine derivatives. Its reaction to form these derivatives depends solely upon the hydrolysis of the cyan group, which does not require the use of a vigorous hydrolyzing agent, to form guanidine.

GUANIDINE NITRATE

Guanidine nitrate is of interest as an explosive and a component of explosive mixtures and as an intermediate in the preparation of nitroguanidine. All other salts of guanidine require strong mixed acids to convert them to nitroguanidine, but the nitrate is converted by dissolving it in concentrated sulfuric acid and pouring the solution into water. Guanidine nitrate is a white granular solid with a melting point of 206°-212° C. It is a stable, non-hygroscopic, and flashless explosive compound: it is readily soluble in alcohol and very readily soluble in water and may be recrystallized from either solvent.

For many years guanidine thiocyanate was the most easily prepared and the most commonly used raw material for the preparation of nitroguanidine by direct nitration with mixed acids. Since, traces of sulfur compounds affect smokeless powder, the nitroguanidine made from the thiocyanate is not entirely satisfactory. Guanidine thiocyanate is also deliquescent, difficult to purify, and generally unpleasant to handle. In 1922, Werner and Bell, in the Journal Of The Chemical Society, reported that dicyandiamide heated with ammonium thiocyanate gives guanidine thiocyanate in a practical yield. This

reaction takes place because the ammonium thiocyanate is readily fusible. This fact suggested to Davis (2) that another ammonium nitrate, which is also readily fusible, might go through the same type of reaction. Davis found that almost theoretical yields of guanidine nitrate can be prepared by using this reaction. This method was developed and used for the preparation of guanidine nitrate.

The method involves heating dicyandiamide and two molecular equivalents of ammonium nitrate. Davis, in his first experiments, used a test tube heated in an oil bath at 160° C. The mass first fused, melted, then became solid. The product was almost entirely guanidine nitrate. An oil bath or some equivalent method of heating should be used, for if the mixture of the two solids is not heated uniformly, decomposition with great evolution of ammonia occurs.

The reaction takes place in two steps. In the first step the ammonium nitrate reacts with the cyan group of the dicyandiamide to form biguanide nitrate, which is the colorless liquid phase of the reaction. The biguanide nitrate then reacts with ammonium nitrate to give crystalline guanidine nitrate. Two molecules of ammonium nitrate are required for every molecule of dicyandiamide.

$$H_2N\text{-}\overset{\overset{NH}{\|}}{C}\text{-}NH\text{-}CN + NH_4NO_3 \longrightarrow H_2N\text{-}\overset{\overset{NH}{\|}}{C}\text{-}NH\text{-}\overset{\overset{NH}{\|}}{C}\text{-}NH_2 \cdot HNO_3$$

$$H_2N-\overset{NH}{\overset{\|}{C}}-NH-\overset{NH}{\overset{\|}{C}}-NH_2 \cdot HNO_3 + NH_4NO_3 \longrightarrow 2\,H_2N-\overset{NH}{\overset{\|}{C}}-NH_2 \cdot HNO_3$$

If an excess of the dicyandiamide is present, the reaction does not go to completion, but leaves a sticky mixture of biguanide nitrate and guanidine nitrate. The ammonia group of the ammonium nitrate is the only portion of the molecule that attacks the cyan group, leaving nitric acid. The intermediate product, biguanide nitrate, is a strong diacid base and the ammonium nitrate involved in its formation supplies only one equivalent of nitric acid. There is, therefore, a point in the early part of the reaction where the biguanide mononitrate tends to attack the ammonium nitrate liberating ammonia. For this reason the process gives a much better yield if an excess of ammonium nitrate is used.

Smith, Sabetta, and Steinbach (16) suggest the same procedure for the preparation of guanidine nitrate using 20 per cent excess ammonium nitrate, resulting in a 87 to 90 per cent yield of guanidine nitrate. They also found that a slight improvement in yield may be effected if half of the ammonium nitrate is fused separately and then the mixture of dicyandiamide and remaining ammonium nitrate is added slowly, each portion being allowed to react before more is added. Shreve and Hunter (15) in a process for the manufacture of guanidine nitrate for use in preparation of aminoguanidine suggest a greater excess of

$$H^2N-\underset{\underset{NH}{\|}}{C}-NH-\underset{\underset{NH}{\|}}{C}-NH^2\cdot HNO^3 + NH^4NO^3 \longrightarrow H^2N-\underset{\underset{NH}{\|}}{C}-NH^2\cdot HNO^3$$

ammonium nitrate than that used by Davis. They found that this excess does not interfere with purifying the product and increases the yield greatly.

The crude guanidine nitrate may either be recrystallized from water or thoroughly dried in its crude state. According to Davis (4), a small amount of ammonium nitrate present in the mixture does not interfere with its conversion to nitroguanidine; the presence of reaction by-products does interfere. Smith, Sabetta, and Steinbach (16) found that the fusion product contains not more than 85 to 87 per cent of guanidine nitrate; the remainder consists of excess ammonium nitrate, unconverted dicyandiamide and "amorphous" material.

In the manufacture of explosives, purity is an important factor. Since the purity of nitroguanidine is directly dependent upon the purity of the guanidine nitrate used in its preparation, it is necessary to have a method for the preparation of pure guanidine nitrate. Presence of moisture in the ammonium nitrate tends to hydrolyze the dicyandiamide to form guanidine, carbon dioxide, and ammonia. These products condense with one another to form ammelide and ammeline. Also the guanidine condenses with itself to form melamine, which is also formed by polymerization of dicyandiamide. Therefore, the three compounds; ammelide, ammeline, and melamine are

among the possible by-products found in the so-called "amorphous" material.

When the "amorphous" material is dissolved in concentrated sulfuric acid and the solution is poured into cold water, it recrystallizes. Therefore, in the preparation of nitroguanidine from the crude fusion product, the "amorphous" material recrystallizes from the sulfuric acid along with the nitroguanidine. The resulting product resembles glass wool instead of the finely crystalline form obtained when pure guanidine nitrate is used. The presence of these impurities affects the chemical properties of nitroguanidine. For example, they decrease the ease of reduction.

By leaching large quantities of crude guanidine nitrate with water a purity of 98.1 per cent can be obtained. Smith, Sabetta, and Steinbach (16) compared the solubility of guanidine nitrate and the "amorphous" material in water, ethanol, and methanol at various temperatures with the following results:

Solvent	Guanidine Nitrate		"Amorphous" Material	
	Temp. °C	g/100cc	Temp. °C	g/100cc
Water	20	25.6	20	0.15
Water	75	42.3	100	1.20
Ethanol	20	4.1	78	0.30
Ethanol	78	15.1		
Methanol	20	4.7	65	0.10
Methanol	64	15.6		

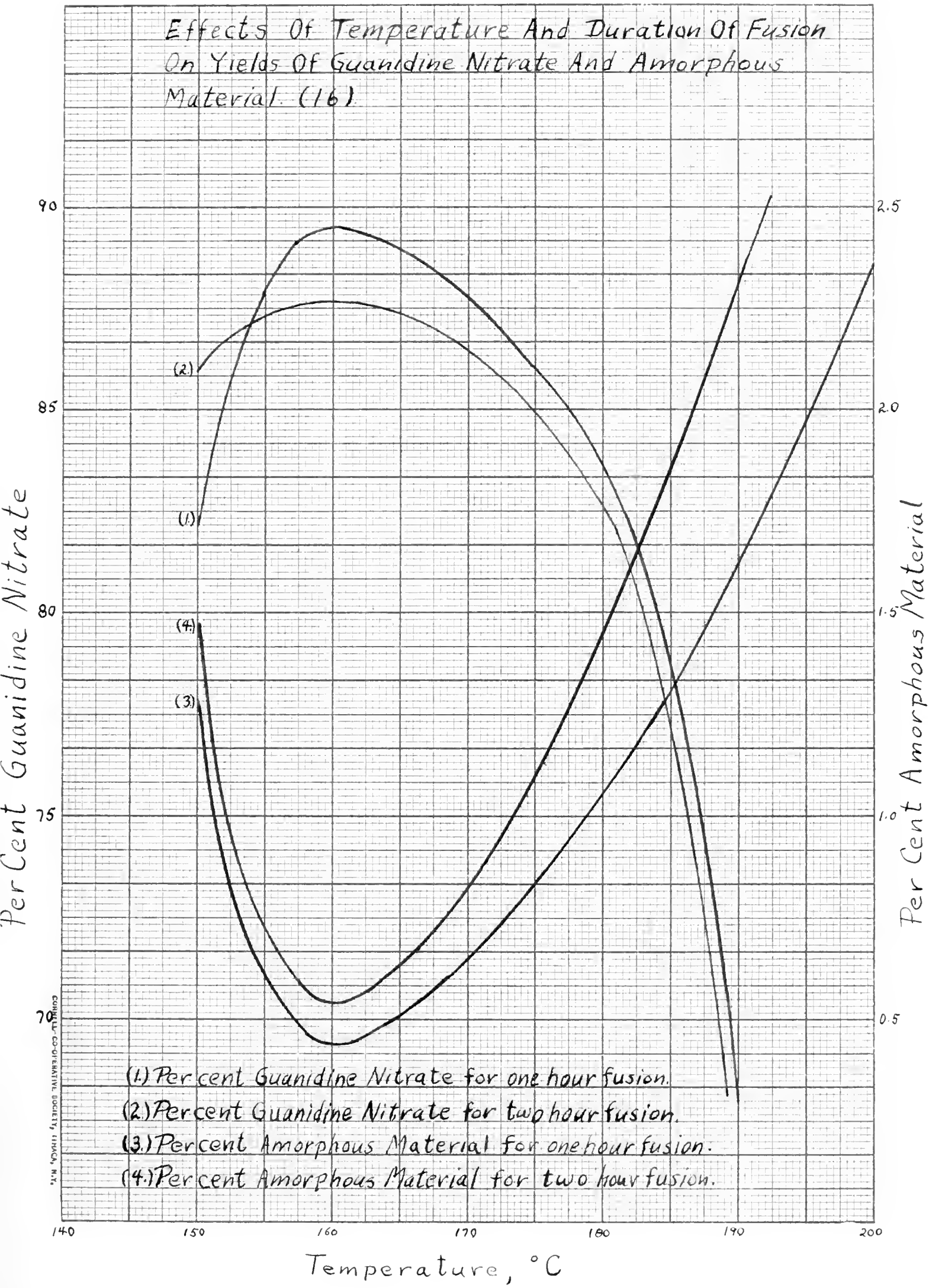
Effects Of Temperature And Duration Of Fusion On Yields Of Guanidine Nitrate And Amorphous Material. (16)
Per Cent Guanidine Nitrate
Per Cent Amorphous Material
Temperature, °C
90
85
80
75
70
2.5
2.0
1.5
1.0
0.5
140
150
160
170
180
190
200
(1.)
(2.)
(3.)
(4.)
(1.) Per cent Guanidine Nitrate for one hour fusion.
(2.) Per cent Guanidine Nitrate for two hour fusion.
(3.) Per cent Amorphous Material for one hour fusion.
(4.) Per cent Amorphous Material for two hour fusion.
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Fig. III

Therefore it can be seen that water at about 20° C could be used for the leaching with good results.

The yield of guanidine nitrate and the amount of "amorphous" material formed is a function of the temperature and the duration of the fusion. Davis found that the best results could be obtained if the temperature was kept at 160° C and the duration of the fusion was about one hour. Smith, Sabetta, and Steinbach (16) proved that this was true by conducting experiments using times of one and two hours for the fusion, at various temperatures. For one-hour fusion at 160° C they got about an 88 per cent yield of guanidine nitrate with about 0.45 per cent "amorphous" material. (Fig. III).

Chemically pure guanidine nitrate may be obtained by using hot water, slightly acidic with nitric acid, for the first recrystallization. This product is the dissolved in cold water and evaporated to half its original volume and crystallized. A third recrystallization from methanol yields pure guanidine nitrate.

Guanidine nitrate is a practical raw material in the production of nitroguanidine and other guanidine derivatives because it is easily prepared and easily converted. It is also non-deliquescent and easily handled.

NITROGUANIDINE

In 1892 Thiele prepared nitroguanidine from guanidine thiocyanate and guanidine nitrate by treatment of each with nitric acid in fuming sulfuric acid. In 1921 Swan and Young (10) conducted experiments on the preparation of nitroguanidine from guanidine nitrate. They concluded that the action of 92 to 95 per cent sulfuric acid on the salt for 48 hours before dilution with water gives the best yields. These investigators used one cubic centimeter of the acid per gram of salt. It has since been found, that if two cubic centimeters of the acid is used to every gram of the salt, the time of the conversion can be cut to about 30 minutes.

The process in the formation of nitroguanidine, from guanidine nitrate by action of sulfuric acid, has been called a dehydration process: actually it is a nitration process. It has been shown by Davis and Underfield (7) that the acid in the guanidine nitrate salt is not attached to a nitrogen atom or an amino group but is attached to the guanidine molecule as a whole. The addition of the concentrated sulfuric acid, which is the "dehydrating" agent, merely causes nitration of the amine group to take place.

$$H_2N\text{-}\overset{NH}{\overset{\|}{C}}\text{-}NH_2 \cdot HNO_3 \xrightarrow{H_2SO_4} H_2N\text{-}\overset{NH}{\overset{\|}{C}}\text{-}NHNO_2 + H_2O$$

In the conversion of guanidine nitrate, it has been

$$H^{+}N-\underset{\underset{NH}{\|}}{C}-NH^{+}\cdot NNO^{-} \xrightarrow{H^{+}/OH^{-}} H^{+}N-\underset{\underset{NH}{\|}}{C}-NHNO^{-} + H^{+}O$$

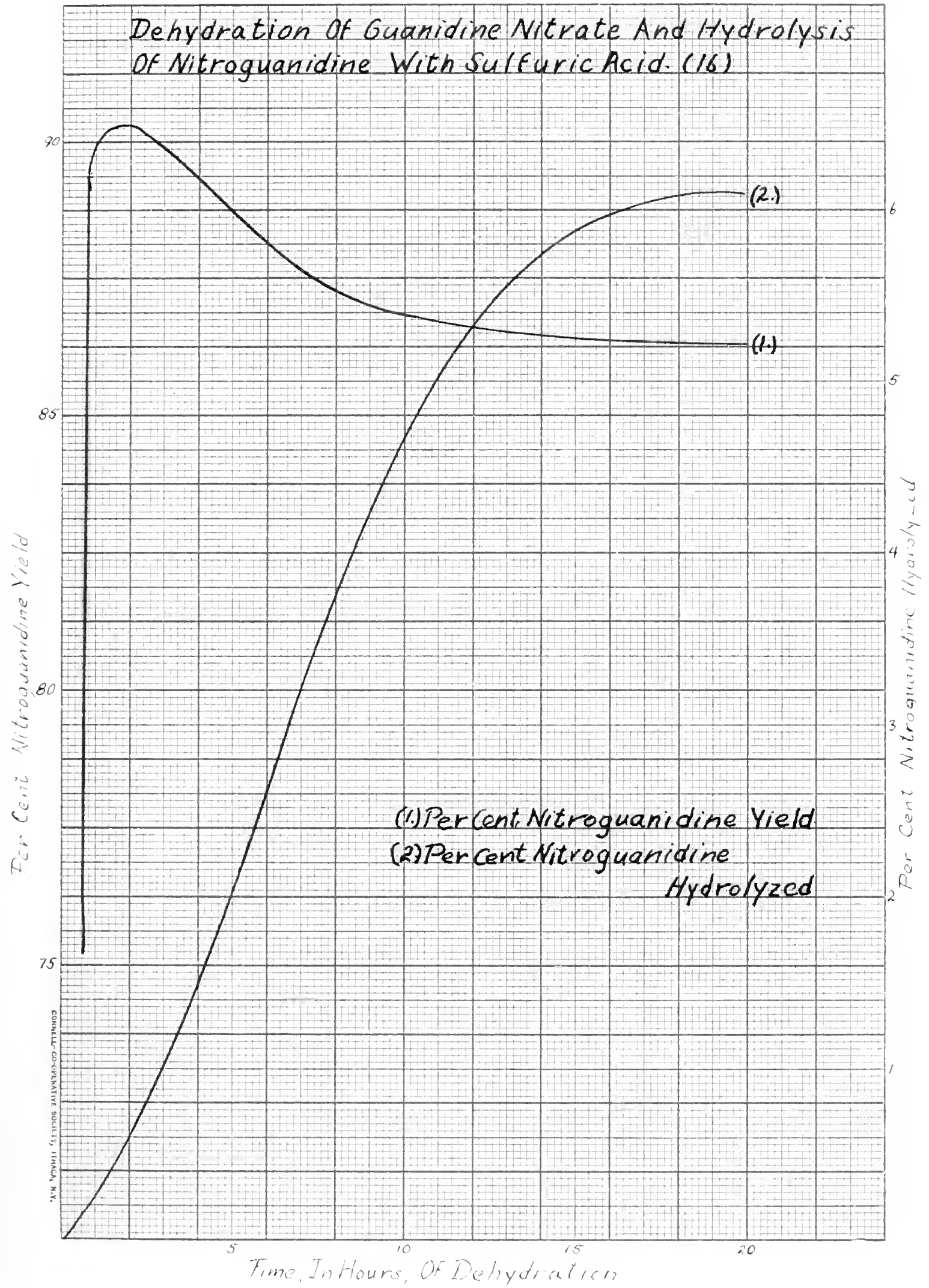

Dehydration Of Guanidine Nitrate And Hydrolysis Of Nitroguanidine With Sulfuric Acid. (16)
90
85
80
75
(2.)
(1.)
6
5
4
3
2
1
(1.) Per Cent Nitroguanidine Yield
(2) Per Cent Nitroguanidine Hydrolyzed
Per Cent Nitroguanidine Yield
Per Cent Nitroguanidine Hydrolyzed
5
10
15
20
Time, In Hours, Of Dehydration
CORNELL CO-OPERATIVE SOCIETY, ITHACA, N.Y.

Fig. IV

found that higher yields of the product are obtained if the nitration period is less than one hour. (16) The conditions necessary for this are that the guanidine nitrate be finely ground and the temperature be regulated. Smith, Sabetta, and Steinbach (16) suggest that the reaction mixture be kept at 0° C or below. However, Shreves and Carter (15) found that the temperature could be allowed to rise to 20° C without apparent change in yield. If a longer time than one hour is used, the sulfuric acid tends to hydrolyze the nitroguanidine. Maximum yields are obtained when the nitration period is limited to one-half to one hour. (Fig. IV) The maximum yield can be raised by using more than the bare minimum of acid. This offers another advantage in that the control of the temperature is made easier.

Nitroguanidine exists in two distinct forms. The alpha form is produced when guanidine nitrate is dissolved in concentrated sulfuric acid and the solution is poured into water. It crystallizes from water in long, thin, flat, flexible, lustrous needles, which closely resemble phthalic anhydride. These crystals are hard and tough and are, therefore, difficult to pulverize. The beta form, with some variable amounts of alpha is produced, by the nitration of the mixture of guanidine sulfate and ammonium sulfate which results from the hydrolysis of dicyandiamide with sulfuric acid. It crystallizes from water in

form-like clusters of small thin elongated plates.

Both forms melt with decomposition at about 272° C; the exact temperature varies from 220° to 250° C with the rate of heating. Both give positive tests for nitroguanidine. Upon reduction both give nitroguanidines of identical properties and both yield identical benzalaminoguanidine nitrates which melt at 161.6° to 162.6° C. Neither form can be converted into the other by solution in water, which presents a convenient method for the separation of the two fractional crystallization. They appear to differ slightly in their solubility in water. The two solubility curves lie close together but apparently cross each other at about 25° C, where the solubility is about 4.4 grams per liter, and also at 100° C, where it is 22.5 grams per liter. Between these two temperatures the beta form seems to be the more soluble.(4)(5)

Neither form appears to be an alpha or pseudo-form of the other, for they have the same solubility in 0.1 N potassium hydroxide. If dissolved in hot concentrated nitric acid and allowed to crystallize, they yield the same nitrate. When allowed to stand in air, the nitrate loses nitric acid slowly yielding the alpha form upon crystallization from water. The similar reaction takes place with hydrochloric acid yielding the alpha form. Chemically the two forms are alike in derivative formation

and color reactions.

There are two qualitative tests for nitroguanidine. Each also gives a positive test with nitroaminoguanidine, but the differences in physical properties of the resulting substances [illegible] [illegible] [illegible] [illegible] [illegible]ished. The procedure for these tests [illegible] [illegible] reference [illegible] or [illegible], p. [illegible].

Nitroguanidine decomposes in two ways as follows:

$$\text{I} \quad H_2N-\overset{NH}{\overset{\|}{C}}-NHNO_2 \rightleftharpoons \underset{\text{cyanamide}}{NH_2-CN} + \underset{\text{nitroamide}}{NH_2-NO_2}$$

$$\text{II} \quad H_2N-\overset{NH}{\overset{\|}{C}}-NHNO_2 \rightleftharpoons NH_3 + \underset{\text{nitrocyanamide}}{H-N=C=N-NO_2}$$

Many of the reactions follow directly from this decomposition. In solution with concentrated [illegible] in [illegible], the first mode of decomposition is followed. When the solution is warmed, nitrogen and nitrous oxide (from dehydration of the nitroamide) first come off; later, carbon dioxide (from the hydrolysis of the cyanamide) is evolved. If the solution is allowed to stand for some time the nitroguanidine and no longer be recovered.

In hot water solution nitroguanidine is [illegible] stable. It has a tendency to decompose in [illegible] especially if an excess of [illegible] the [illegible] decomposition is [illegible]. [illegible] prolonged [illegible] filtrations, the solution may tend to become [illegible]. The presence of the [illegible] tends to [illegible] the nitroguanidine

and also inhibits the second mode which produces the amount . However, if the solution is warmed to vigorous amount the second type of decomposition takes place slowly.

When heated upon melting, nitroguanidine decomposes and triazolone cannot be obtained as a liquid. The products formed from the decomposition are those which would be expected from the rearrangement. In all, there are about twenty one substances formed, all of which are polymers or decomposition products of the rearrangement products. 11 of these substances have been detected in, or isolated from, the products of the decomposition by heat.

Nitroguanidine is used in explosives as a constituent in flashless smokless powder, usually in conjunction with nitrocellulose. The powder containing it produces a considerable amount of gray white smoke on of solid materials from the decomposition of the explosives. The gases given off smell of ammonia. The powders produces more smoke than the usual flashless powders.

Nitroguanidine is also a "cool" explosive, that is, the temperature of explosion is low. There seems to be some disagreement as to the exact temperature however. Vieille and Petart, separately determined it to be 2070° C. Petart, however, found that the pressures exerted by the

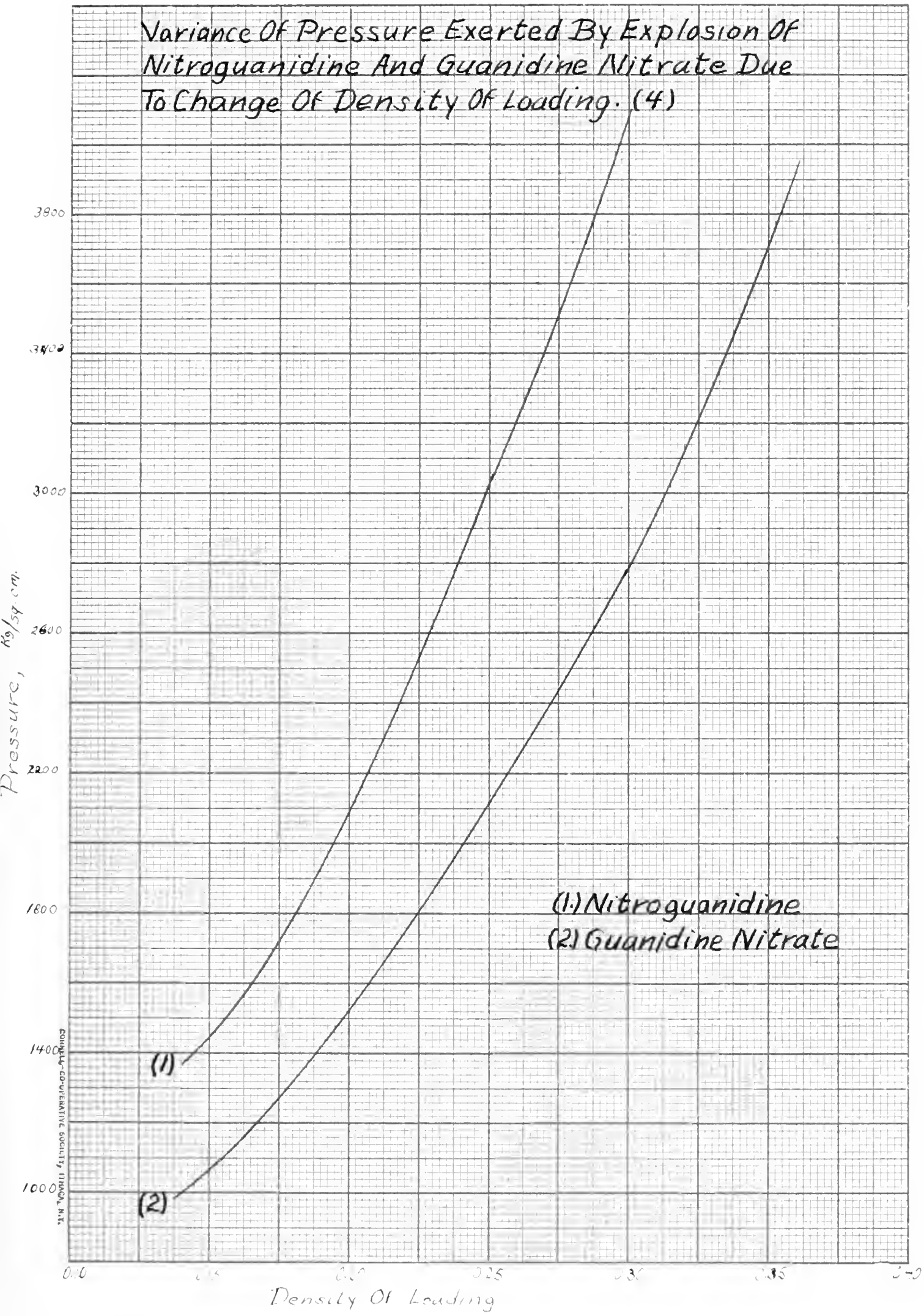

Variance Of Pressure Exerted By Explosion Of Nitroguanidine And Guanidine Nitrate Due To Change Of Density Of Loading. (4)
3800
3400
3000
2600
2200
1800
1400
1000
Pressure, Kg/sq. cm.
(1)
(2)
(1.) Nitroguanidine
(2) Guanidine Nitrate
0.0
0.25
0.35
Density Of Loading
CORNELL CO-OPERATIVE SOCIETY, ITHACA, N.Y.

Fig. V

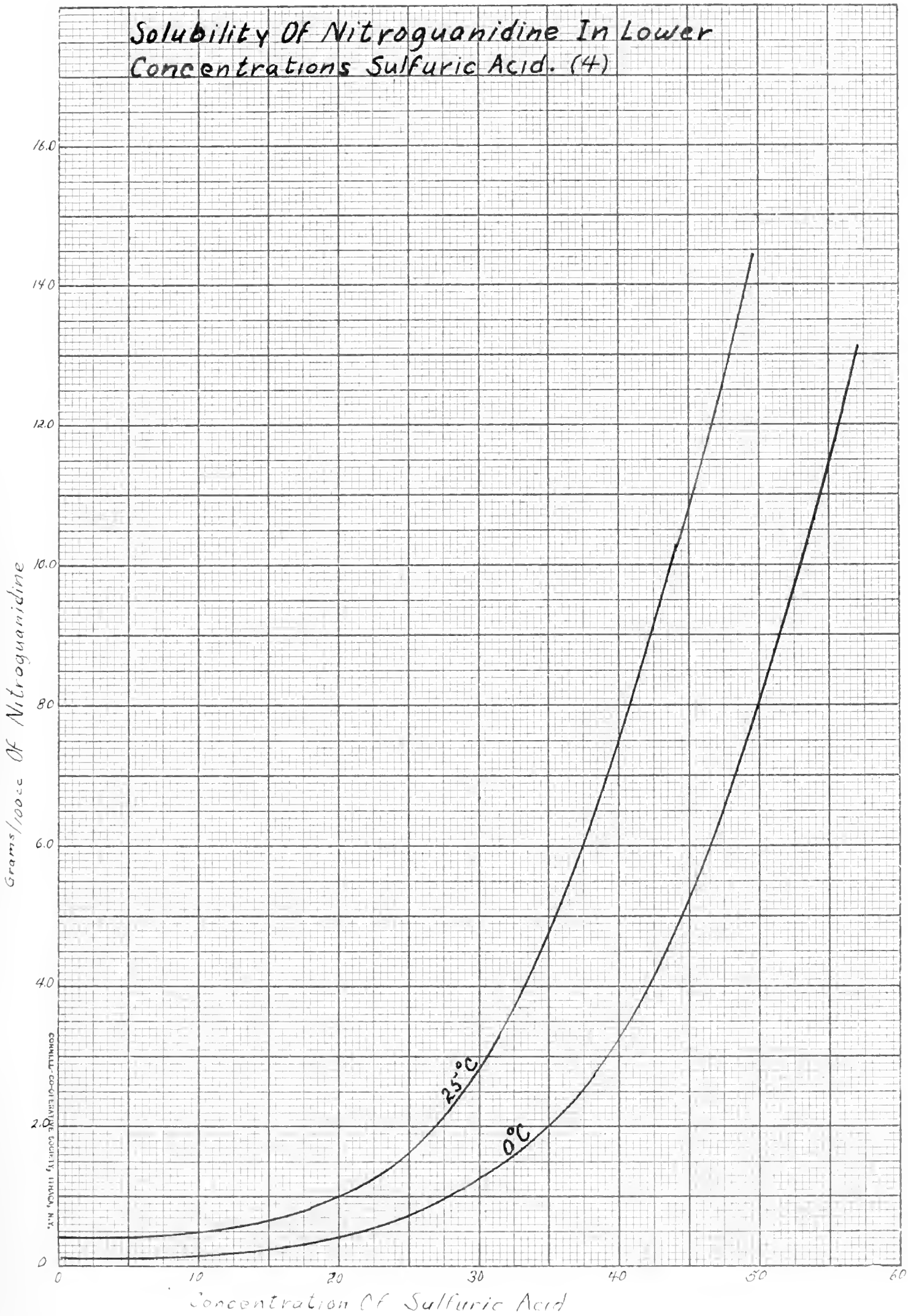

Solubility Of Nitroguanidine In Lower Concentrations Sulfuric Acid. (4)
Grams/100cc Of Nitroguanidine
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0
25°C
0°C
0
10
20
30
40
50
60
Concentration Of Sulfuric Acid
CONNELLY-CONGDON LITHOGRAPHING COMPANY, UTICA, N.Y.

Fig. VI

explosion of nitroguanidine and also guanidine nitrate, varies considerably with the density of loading (Fig. V), he therefore believed that his calculated explosion temperature was too low. Cater, Sarasror and Curie found that Stettbacher's hypothesis was correct. They found the explosion temperature to be 177°C. Due to this "cool" explosion, very little gun erosion is caused by nitroguanidine.

Alpha nitroguanidine is the form most commonly used in explosives. In its production from guanidine nitrate, concentrated sulfuric acid is used. Since the nitroguanidine is somewhat soluble in moderately concentrated acid (Fig. VII), the reaction must be rather highly diluted if the recovery is to be satisfactory. In the process of recrystallization of the alpha nitroguanidine from water, rapid cooling of the solution produces small needles that dry out to a fluffy mass which is too coarse to be used in colloided powders. To procure an extremely fine powder suitable for use, the hot solution may be sprayed against a cooled surface from which the water is removed, or the solution may be dried in a spray dryer.

ALKYL-NITROGUANIDINES

In general, the alkyl nitroguanidines are colorless crystalline solids, moderately soluble in alcohol, insoluble or slightly soluble in cold water(more soluble in hot), and insoluble or slightly soluble in ether. Their properties are similar to those of nitroguanidine.

Preparation of the alkyl-nitroguanidines involves a reaction between nitroguanidine and the appropriate amine. The reaction originates from the rearrangement of nitroguanidine. As shown before, nitroguanidine decomposes either to form cyanamide and nitroamide or to form urea and nitrocyanamide. When an aqueous solution of nitroguanidine is treated with an amine a small amount of alkyl guanidine, a considerable amount of alkyl-substituted urea, and much alkyl-nitro guanidine are produced. The alkyl guanidine is formed from the action of the amine on the cyanamide produced from the first mode of rearrangement. The alkyl-substituted urea is formed by the hydrolysis of nitroguanidine to nitro urea which then further decomposes to cyanic acid, which reacts with the amine. The alkyl-nitroguanidine is formed by the action of the amine on the nitrocyanamide produced from the second mode of rearrangement.

$$HNCN\text{-}NO_2 + RNH_2 \longrightarrow RNH\text{-}\overset{NH}{\overset{\|}{C}}\text{-}NHNO_2$$

In the process, slightly more than one molecule of nitroguanidine is used to a 10 per cent aqueous solution of the primary amine. The mixture is heated to 60°-70° C until all of the nitroguanidine disappears. Ammonia comes off abundantly, showing that the second mode of decomposition takes place. The solution is then cooled and filtered, and the filtrate is evaporated to dryness. The residue is extracted with alcohol at 70° . Upon cooling, the fairly pure alkyl-nitroguanidine crystallizes out in yields varying from 70 to 50 per cent of the theoretical.

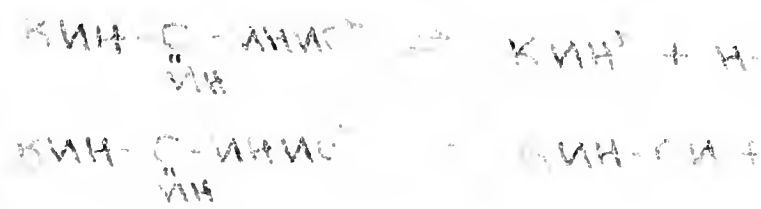
Considerable work had been done by Davis and Luce (8) on various alkyl-nitroguanidines. They found that dimethyl amine is the only secondary amine which reacts successfully. It requires a more vigorous treatment than the primary amines. A more concentrated solution of the amine is required, also a higher temperature or a longer time, to cause the nitroguanidine to go into solution with the amine.

The alkyl-nitroguanidines undergo a decomposition similar to nitroguanidine. (7)

$$\text{I} \quad RNH\text{-}\overset{NH}{\overset{\|}{C}}\text{-}NHNO_2 \rightleftharpoons RNH\text{-}CN + NH_2\text{-}NO_2$$

$$\text{II} \quad RNH\text{-}\overset{NH}{\overset{\|}{C}}\text{-}NHNO_2 \rightleftharpoons RNH_2 + H\text{-}N{=}C{=}N\text{-}NO_2$$

The second mode is that by which it is prepared from nitroguanidine. The reaction takes place in dilute

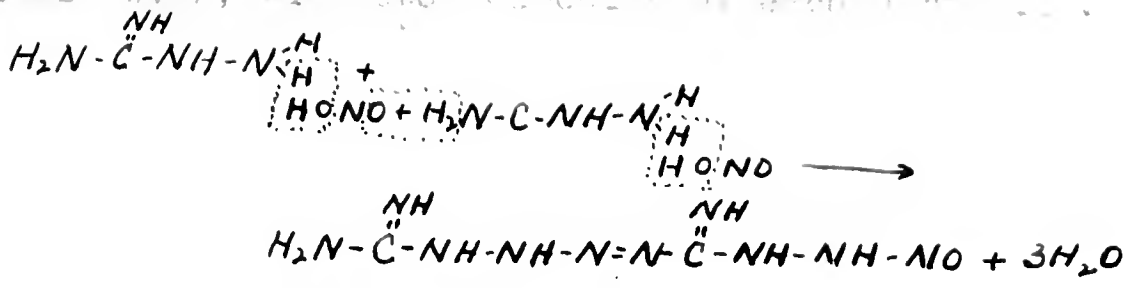


solution with a decomposition of the nitrocyanamide to cyanic acid and nitrous oxide. The first mode is followed in acid solution with a pH of about 6.17. This opens possibilities for the preparation of mono-alkyl, and N, N'-dialkyl guanidines. The pH is regulated usually with acetic acid. Ammonia or a primary amine then react with the alkyl cyanamide to form mono-alkyl or N, N'-dialkyl guanidines respectively. A fairly good yield can be obtained in either case. In each mode of decomposition some alkyl urea is present because of the hydrolysis of the alkyl-nitroguanidine.

The alkyl guanidines may be nitrated by the same procedure as is used in the preparation of nitroguanidine from guanidine nitrate. The alkyl guanidine salt of nitric acid is "dehydrated" or nitrated by dissolving it in sulfuric acid and pouring into cold water. There are some limitations, however: nitration does not take place on a nitrogen atom to which an alkyl group is attached nor on the imine nitrogen. Therefore, N, N'-dialkyl or N, N', N"-trialkyl guanidines cannot be nitrated.

Tetrazene

Tetrazene is the common name of [illegible] - [illegible] guanylidene-nitrosaminoguanyl tetrazene. Hoffman and [illegible] [illegible] studied it [illegible] and determined its structure by its [illegible] reaction. It is formed [illegible] action of nitrous acid on aminoguanidine, in the presence of nitrous salts, with two molecules of [illegible].



Tetrazene is a colorless or pale yellow glassy material. It is practically insoluble in water, alcohol, ether, benzene, and carbon tetrachloride. The density in its ordinary form is only 0.45, but when compressed into a pellet at [illegible] pounds per square inch it has a density of 1.25. It is soluble in strong hydrochloric acid solution, forming the hydrochloric salt. Treatment of the salt with a alkaline substance, as sodium hydrate or ammonia, recovers it to tetrazene. It is slightly hygroscopic. It forms explosive salts with [illegible] the two most [illegible] are the perchlorate and the [illegible] salt formed by an excess of silver nitrate. Tetrazene, both wet and dry, is stable at ordinary temperatures, but decomposes when boiled with water, to evolve the gases

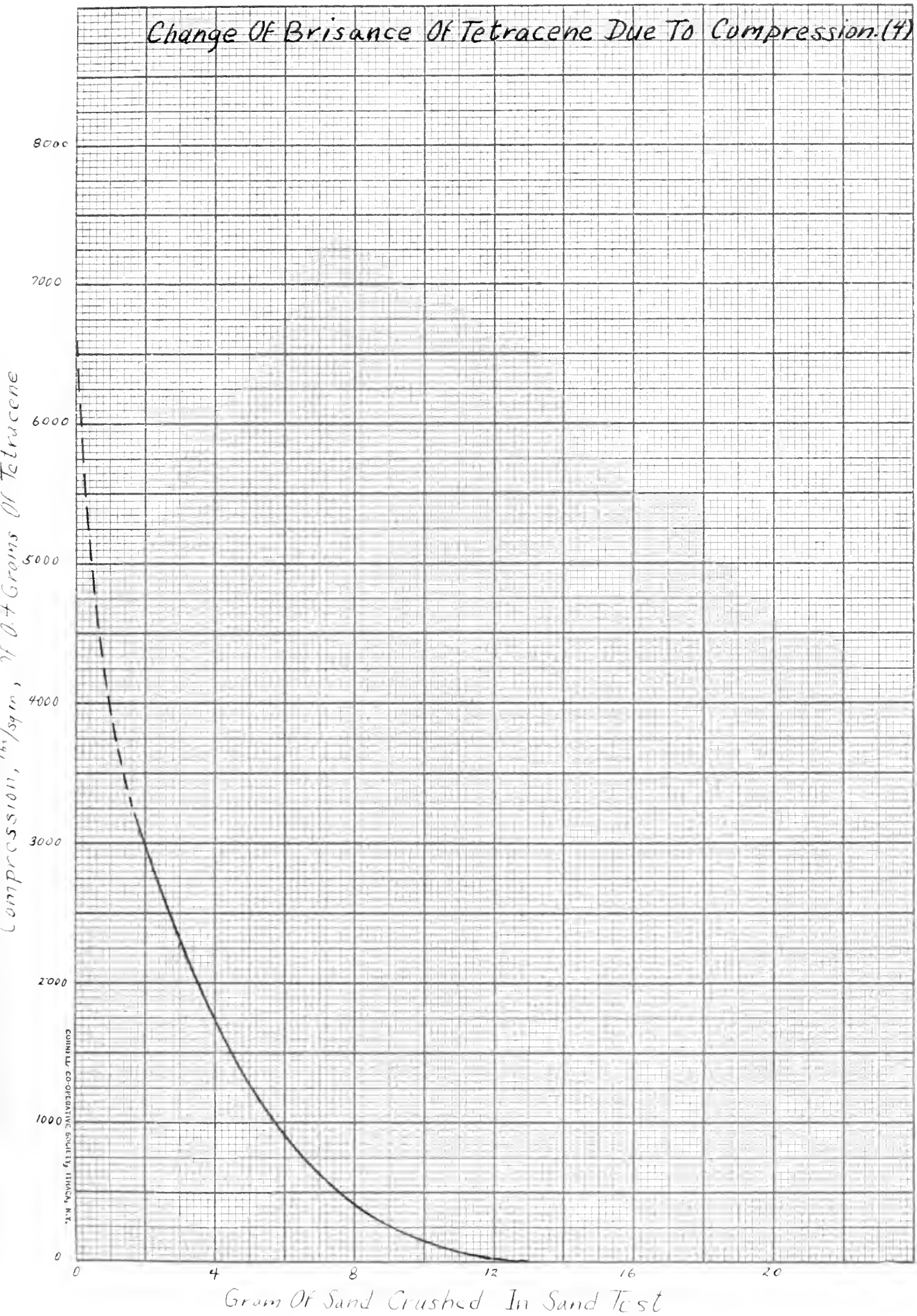

Change Of Brisance Of Tetracene Due To Compression.(4)
Compression, lbs/sq in, Of 0.4 Grams Of Tetracene
8000
7000
6000
5000
4000
3000
2000
1000
0
0
4
8
12
16
20
Gram Of Sand Crushed In Sand Test
CORNELL CO-OPERATIVE SOCIETY, ITHACA, N.Y.

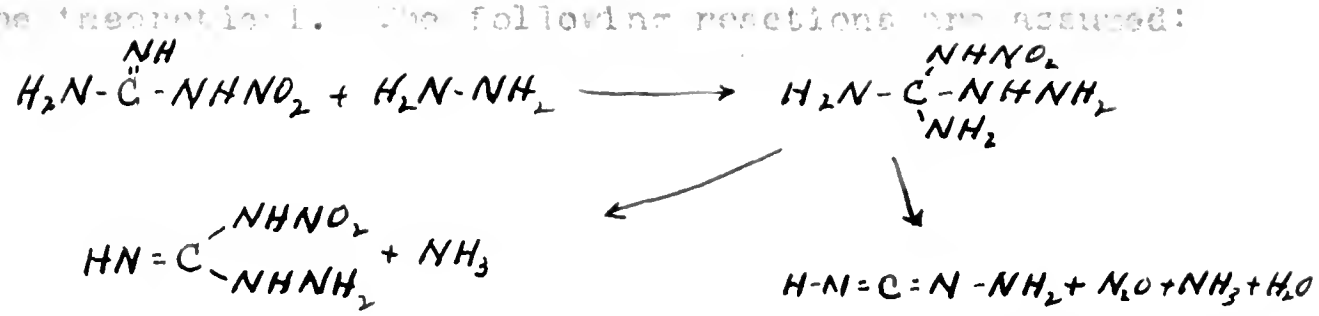
Fig. VII

of nitrogen per mole of tetracene. It can be hydrolyzed with caustic to yield ammonia, cyanamide, and trinitroaminoguanidine, which can be isolated as an explosive copper salt by the addition of copper acetate.

Tetracene explodes readily from flame with the production of much black smoke and very little noise. It is slightly more sensitive to impact than lead azide, is fulminate. The brisance of tetracene is the one test when it is not compressed. Figure [illegible] shows the change of brisance with compression when 0.4 grams of tetracene are used in the sand test. (4, p. 402) It is easily "dead pressed", that is, compressed to the point at which it no longer will detonate. Since self-acceleration is low, it is not suitable for use alone as an initiating explosive. It is as efficient as fulminate only if it is externally initiated. These properties make it useful only as a component in a mixture for detonators, a booster, or mixtures with a primary explosive to increase its sensitivity to heat or flame. British practice recommends a mixture of tetracene and lead azide for explosive rivets.

FREE GUANIDINE NITROGEN DERIVATIVES

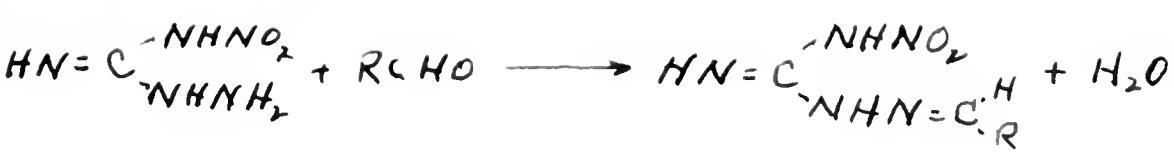
<u>Nitro-aminoguanidine</u>. The first work on nitro-aminoguanidine was done by Phillips and Williams (13) at the University of Buffalo. While working with guanidine compounds they found that an interesting substance is formed when nitroguanidine is heated with a solution of hydrazine. They obtained a yield of about 50 per cent of the theoretical. The following reactions are assumed:

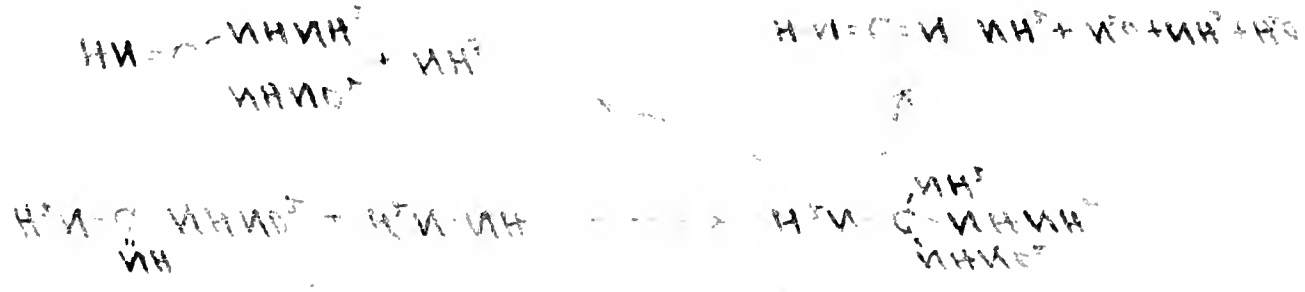


The compound is a white crystalline powder, soluble in water to the extent of 0.74 per cent at 20° C and 7.0 per cent at 70° C, and insoluble in most organic solvents. It melts at 166° C with an explosion, but may be heated in a vacuum without detonation. When ignited, each separate particle explodes as it becomes ignited leaving a yellow, insoluble residue.

Two aldehydes and ketones are added to a hot aqueous solution of nitro-aminoguanidine, a crystalline precipitate forms. The reaction is assumed to take place in the following manner:

Ketones:





[illegible] condensation products of [illegible] ketones [illegible]. [illegible] of the [illegible] of the nitro [illegible] hydro-[illegible].

[illegible] compounds [illegible] [illegible] [illegible] [illegible] explodes [illegible] [illegible] detonate [illegible] [illegible] [illegible] [illegible]

$$H_2N\text{-}\overset{\overset{NH}{\|}}{C}\text{-}NHNH_2 + HONO \longrightarrow N_3\text{-}C{=}{}^{NH}_{NH_2} + 2H_2O$$

It forms salts with acids. It was first isolated as the nitrate. The nitrate is not used as an explosive. The picrate and the perchlorates explode violently by shock and heat.

<u>Guanidine picrate</u>. Guanidine picrate is the addition product of guanidine and picric acid. It is a yellow crystalline solid which melts with decomposition at about 290° C. It is an explosive compound which is even less sensitive to shock than is ammonium picrate. Its detonation rate, at a density of 1.50, is 6000 meters per second. It is used in armor-piercing shell and, with other explosives, to make them less sensitive to heat and shock.

<u>Nitroaminoguanidine</u>. Nitroaminoguanidine is made by the partial reduction of nitroguanidine. The reaction is carried out in the presence of zinc, ammonium chloride and water.

$$H_2N\text{-}\overset{\overset{NH}{\|}}{C}\text{-}NHNO_2 + 2[H] \longrightarrow H_2N\text{-}\overset{\overset{NH}{\|}}{C}\text{-}NHNO + H_2O$$

The temperature of the reaction should not exceed 40°-50° C. and the mixture should be stirred constantly. At the completion of the reaction, the mixture is filtered. The residue contains nitroaminoguanidine, zinc oxide or hydroxide, and basic zinc chloride. The nitroaminoguani-

dine can be extracted with water at 60° C, and recrystallized from the water by stirring at 0°. By this method a yield of about 42-52 per cent of the theoretical can be obtained.

Nitrosoguanidine is a cool and flashless military explosive. It is a pale yellow crystalline powder which melts at 160° with rapid decomposition. It is very sensitive to shock, friction, and heat, and decomposes in water at ordinary temperatures. It explodes on contact with sulfuric acid. For these reasons it is impractical as an explosive.

Nitrosoguanidine decomposes in water similar to nitroguanidine. The main mode of decomposition is to nitrosoamide and cyanamide. Upon heating of the aqueous solution, the nitrosoamide breaks down into water and nitrogen, and the cyanamide polymerizes to dicyandiamide.

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